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(54) IMPROVEMENTS IN OR RELATING TO THE MANUFACTURE OF SHAPED ARTICLES OF CALCIUM SULPHATE DIHYDRATE

(71) We, SALZGITTER INDUSTRIEBAU G.m.b.H., of 332 Salzgitter 41, Germany, a German Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a method for the manufacture of shaped articles of calcium sulphate dihydrate from calcium sulphate hemihydrate (usually referred to simply as "hemihydrate"), particularly from α-calcium sulphate hemihydrate, by compressing a mixture of water and calcium hemihydrate into suitable shapes.

The many technical uses of gypsum ($CaSO_4.2H_2O$) are based essentially upon the ability of partially dehydrated gypsum, naturally-occurring gypsum or synthetic gypsum as obtained for example in wet phosphoric acid manufacture, boric acid manufacture and waste gas desulphurization, to set into a hard solid mass after a short time, when mixed with water to give a castable thick slurry. Methods for the manufacture of shaped articles from gypsum or anhydriate are widely known. Shaped articles of gypsum are manufactured by casting a pourable mass of calcium sulphate hemihydate and water in suitable moulds and then subjecting the cast articles to a drying process. For this purpose, calcium sulphate hemihydrate is mixed with a predetermined amount of water corresponding to the "green" density required, a setting accelerator usually being added to the mixing water. On completion of the mixing process, the hemihydrate mix is charged into moulds, the mould covers are applied and the excess liquid hemihydrate mix is removed. The initial hardening process of the hemihydrate mix, with the technologically important times, such as the initiation of setting, the end of setting and the end of hydration as well as the intermediate stages, essentially determine the course of the process of production and thus to an extent the economics of the process. In plaster production, it is necessary constantly to adjust the setting properties of the final product, plaster (hemihydrate) or anhydrite, by means of material or technological measures. It is known however that it is very difficult to achieve constant product quality, since, apart from influences from the calcining process of the gypsum rock, transport conditions for instance can also affect the setting properties of the product. Therefore, it is sometimes necessary to wait 30 to 45 minutes from the initial introduction of the hemihydrate mix in the mixing vessel until removal of the shaped articles, because the setting is very slow. In the established manufacturing method, there is also the problem of economical drying of the moist product since, in general, artificial drying may take up to 48 hours. The long drying time is required partly because, with gypsum product temperatures of over 100°C., dehydration of the dihydrate formed proceeds rapidly and damages the products. With increasing product thicknesses, drying costs in many cases exceed the moulding costs and are not infrequently twice as high.

This means that the course of the hardening of the hydrated moist products, during drying between the end of hydration and the achievement of constant mass, passes through a limit which lies at a moisture content of about 4% to 5% by weight, relative to calcium sulphate dihydrate. Beneath this limit, the dissipation of moisture is unduly slow, so that the cost of drying within this residual moisture range rises considerably. Previously, there have been many attempts to simplify the manufacture of these products, particularly by curtailing the process of drying of moist products, in order to reduce the considerable capital and operating costs. These attempts have not proved to be satisfactory, however.

The invention provides a method for the manufacture of shaped articles from calcium sulphate hemihydrate, in particular α-calcium sulphate hemihydrate manufactured by the hydrothermal conversion of chemical waste gypsum, in which in addition to a substan-

tially more rapid and simple manufacture of shaped articles, the capital-intensive, time-consuming drying process is dispensed with, so that the range of applications of chemical waste gypsum, which is available in vast quantities, is considerably enlarged.

According to the invention, the drying problem is solved by carrying out manufacture of the shaped articles by compressing in a mould a mixture of calcium sulphate hemihydrate and a weight of water which is not more than the stoichiometric weight required for hydration of the hemihydrate to calcium sulphate dihydrate.

It has been found that the previously stated problems can thus be solved in their entirety. The advantage is thus gained that, with the addition of the prescribed amount of water, which in using α-calcium sulphate hemihydrate can be effectively incorporated into this α-calcium sulphate hemihydrate before or after giving it the desired moulded shape by compression, shaped articles are produced having sufficient initial crushing strength to enable them to be stacked or transported. The drying process becomes completely superfluous, so that plant and operating costs are considerably reduced. It has been found that the shaped articles manufactured according to the invention, in contrast to the products obtained with the known manufacturing processes, can be built up and rendered, for example, three hours after manufacture.

According to a preferred embodiment of the invention, a mixture containing less than the stoichiometric weight of water is used and the residual weight of water stoichiometrically necessary is applied to the shaped articles after they have been moulded. The residual weight of water is preferably applied to the articles by spraying.

According to a further preferred feature of the invention, the compression step is effected at a pressure in the range from 3 to 650 kp/cm², preferably 30 to 250 kp/cm². (1 kp = 1 kilopond, so that a pressure of 1 kp/cm² is equivalent to a force of 1 kg/cm², which is also equivalent to 0.0703 psi.)

In using calcium sulphate hemihydrate obtained by the hydrothermal method, it is of particular advantage if, according to a further preferred feature of the invention, the mixture used for manufacturing the shaped articles is formed at a temperature of 45° to 90°C. In this way, the otherwise necessary cooling of the calcium sulphate hemihydrate obtained by the hydrothermal method is rendered unnecessary.

If shaped articles are manufactured by the application of a pressure of 3 to 650 kp/cm² and from α-calcium sulphate hemihydrate containing approximately 10% by weight of water, which after removal from the moulds are subjected to a spraying process and are thus treated with the measured amount of water necessary to achieve hydration, then in an immediately subsequent method step, these "green" shaped articles can be stacked or transported, because of their high initial strength of e.g. 40 kp/cm² (= 600 psi). It is also possible with advantage to supply the freshly-pressed shaped articles with so much water by the measuring spray device that the final moisture content is in the range of up to 20% by weight, preferably 5% by weight, above the theoretical stoichiometric amount of water.

Since α-calcium sulphate hemihydrate manufactured according to the known hydrothermal method is produced at temperatures between 90° and 100°C., the method according to the invention can be carried out with considerable success using hot α-calcium sulphate hemihydrate containing the residual water required for its manufacture. Since α-calcium sulphate hemihydrate is generally produced with 6% to 12% by weight of adhering water, only very little or even no water need be additionally provided for shaping by pressing. Preferably, the hot moist α-calcium sulphate hemihydrate is cooled on a cooling belt or in a cooling screw conveyor to a temperature below 80°C before compression moulding. If for example the water content of the freshly-produced α-calcium sulphate hemihydrate is very low, in many cases cooling by means of the added mixing water is sufficient.

According to a further embodiment of the invention, a granular filler material is included in the mixture for the manufacture of shaped articles in a proportion up to 20% by weight and preferably 5% to 10% by weight based on the total dry mix. Examples of fillers include sand, quartz dust or the like. In contrast to the known method, a considerable increase in strength of the shaped articles so manufactured is surprisingly achieved in this way. It has surprisingly been found that α-calcium sulphate hemihydrate mixed with approximately 10% by weight of water, after compression at pressures of about 10 kp/cm², gives shaped articles of sufficient adge stability, that is to say not even the edges of freshly-moulded articles are likely to suffer damage in normal handling. The shaped articles are already so stable after removal from the moulds that they can be sprayed directly with the amount of water required. Since compression-moulding of the mixture according to the invention may take place directly after the short mixing time and the operative speed of the press can be adjusted, for example, to two cycles per minute, the size of a plant for a predetermined capacity is substantially decreased as compared with known methods.

The initial crushing strength of the shaped

articles manufactured according to the above method, with a forming pressure of 10 kp/cm², for example, lies between 30 and 50 kp/cm². It has also been found that the speed of reaction of the α-calcium sulphate hemihydrate is surprisingly considerably increased, by hot compression with an amount of water, according to the invention, less than is necessary for complete hydration, which partly explains the high initial strength.

A further advantage of the method described is that the shaped articles produced are frost-resistant both immediately after formation and immediately after application of the residual amount of water necessary for complete hydration. In contrast, shaped articles manufactured from α-calcium sulphate hemihydrate according to the known casting method are effectively frost-resistant only after extensive drying and even then only at a water saturation value ≤ 0.85.

The following Examples will serve for explaining the present invention.

EXAMPLE 1

A mass of 17.8 kg of hot α-calcium sulphate hemihydrate at 90°C with an initial as-manufactured water content of 6% by weight was mixed with 0.53 kg water in a blade mixer and the 60°C hot compression mass was moulded under a pressure of 5 kp/cm² into a block 400 × 400 × 100 mm in size.

After removal from the mould, the block was sprayed via a spraying device with 1.71 kg water and was then left to stand under normal conditions. The initial crushing strength of the block amounted to 40 kp/cm², whereas the crushing strength after storage for 24 under normal conditions at a "green" density of 1.32 g/cm³ amounted to 225 kp/cm².

EXAMPLE 2

A mass of 25.25 kg of 80°C hot α-calcium sulphate hemihydrate with an initial as-manufactured water content of 11.5% by weight was cooled to 60°C and the warm mass was compressed under pressure of 500 kp/cm² into a block with dimensions 400 × 400 × 100 mm. After removal from the mould, the block was sprayed with 1.70 kg water and was then allowed to stand under normal conditions.

The initial crushing strength of the block amount to 60 kp/cm², whereas the crushing strength after storage for 24 hours under normal conditions at a "green" density of 1.87 g/cm³ amounted to 550 kp/cm².

EXAMPLE 3

A mass of 17.15 kg of 90°C hot α-calcium sulphate hemihydrate with an as-manufactured water content of 6% by weight and 0.96 kg of sand was mixed with 0.69 kg of water in a mixer and the 60°C hot mouldable mass was then compressed under a pressure of 5 kg/cm² into a block measuring 400 × 400 × 100 mm.

After removal from the mould, the block was sprayed with 1.47 kg of water and was then allowed to stand under normal room conditions.

The initial crushing strength of the block amounted to 48 kp/cm², whereas the crushing strength after storage for 24 hours under normal conditions at density of 1.33 g/cm³ amounted to 305 kg/cm².

WHAT WE CLAIM IS:—

1. A method for the manufacture of shaped articles of calcium sulphate dihydrate, which comprises compressing in a mould a mixture of calcium sulphate hemihydrate and a weight af water which is not more than the stoichiometric weight required for hydration of the hemihydrate to calcium sulphate dihydrate.

2. A method according to claim 1, in which a mixture containing less than the stoichiometric weight of water is used and the residual weight of water stoichiometrically necessary is applied to the shaped articles after they have been moulded.

3. A method according to claim 2, in which the residual weight of water is applied by spraying.

4. A method according to claim 1, 2 or 3, in which the compression step is effected at a pressure in the range from 3 to 650 kp/cm².

5. A method according to claim 4, in which the pressure used is from 30 to 250 kp/cm².

6. A method according to any preceding claim, in which the calcium sulphate hemihydrate used is α-calcium sulphate hemihydrate.

7. A method according to any preceding claim, in which the mixture used for manufacturing the shaped articles is formed at a temperature of 45° to 90°C.

8. A method according to any preceding claim, in which the mixture used for manufacturing the shaped articles includes a granular filler in a proportion up to 20% by weight.

9. A method according to claim 8, in which the filler comprises 5% to 10% by weight of the mixture.

10. A method according to claim 1, substantially as hereinbefore described.

11. A shaped article of calcium sulphate dihydrate, when made by a method according to any preceding claim.

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